NASA
TP
2295
c.1

Ultra-High Molecular Weight Silphenylene-Siloxane Polymers
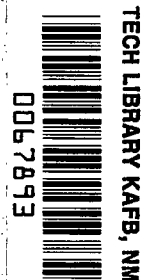
W. J. Patterson,
N. H. Hundley,
and L. M. Ludwick

NASA

**NASA
Technical
Paper
2295**

1984

Ultra-High Molecular Weight Silphenylene-Siloxane Polymers

W. J. Patterson,
N. H. Hundley,
and L. M. Ludwick

*George C. Marshall Space Flight Center
Marshall Space Flight Center, Alabama*

TABLE OF CONTENTS

LIST OF ILLUSTRATIONS

LIST OF TABLES

ULTRA-HIGH MOLECULAR WEIGHT SILPHENYLENE-SILOXANE POLYMERS

I. INTRODUCTION

The need to develop high-temperature elastomers that will perform in extreme thermo-oxidative environments is widely recognized. Long-term thermal, hydrolytic and oxidative stability as well as retention of mechanical properties are sought for these materials. A logical starting point for this development is the silicone polymers with their inherent thermal/oxidative stability. Substantial prior research in this laboratory has been directed toward a class of aryl-modified siloxane polymers designated as silphenylene-siloxane [1-3]:

$$\left(\begin{array}{c} CH_3 \\ | \\ Si \\ | \\ CH_3 \end{array} - \left\langle \bigcirc \right\rangle - \begin{array}{c} CH_3 \\ | \\ Si - O - \\ | \\ CH_3 \end{array} \begin{array}{c} CH_3 \\ | \\ Si - O \\ | \\ CH_3 \end{array} \right)_n$$
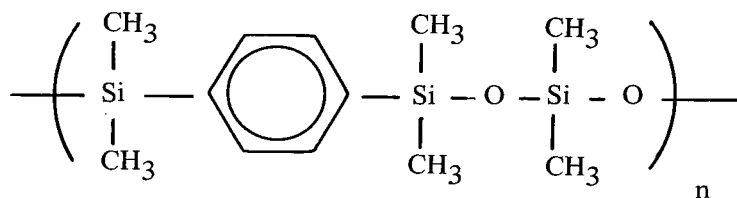
(Polysilphenylene-siloxane)

These polymers were synthesized via an aminosilane/silanol polycondensation with weight average molecular weights ($\overline{M}_w$) typically limited to 1 to 2 x 10^5. Recent studies 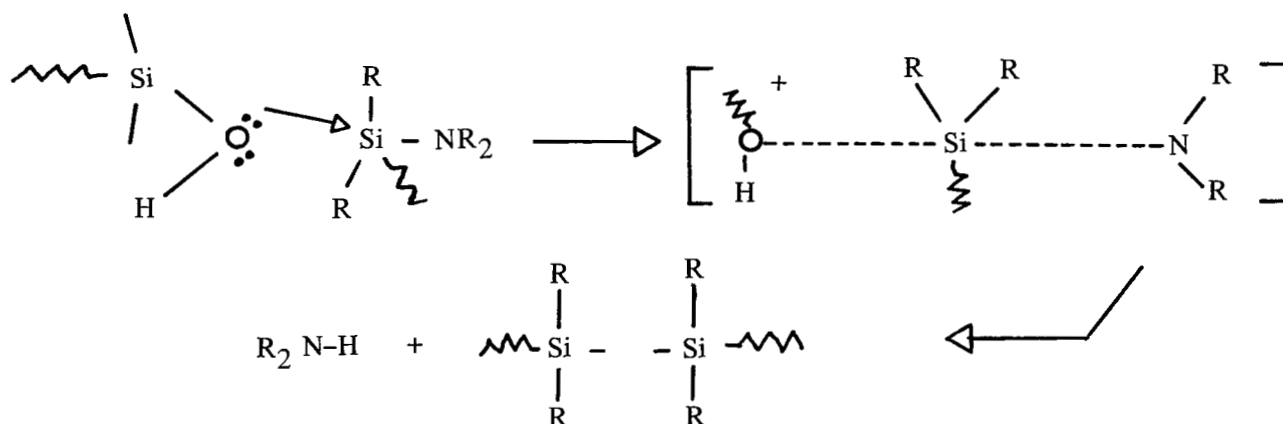[4] with an analogous carborane-siloxane system utilizing a high reactivity monomer and multi-staged polymerization indicated greatly increased molecular weights (approximately 10^6) and corresponding improvements in mechanical properties and thermal stability. This improvement was attributed to increased regions of entanglement of the substantially longer polymer chains.

Therefore the thrust of this research study was to utilize the silphenylene-siloxane (SPS) polymer as a model to assess (1) higher reactivity monomers, and (2) multi-stage polymerization techniques to attain weight average molecular weights approaching 10^6.

II. POLYMER DEVELOPMENT

A. Monomer Reactivity Considerations

The basic polymer-forming reaction leading to the SPS structure involves nucleophilic displacement at silicon. This type reaction has been described by Sommer [5] as having an S_N2-like mechanism, implying a bimolecular mechanism with back or flankside attack by the nucleophile (silanol) on the aminosilane substrate:

The reaction scheme at the top of the page shows a pentacoordinate transition state mechanism for the aminosilane/silanol polycondensation.

The participation of 3d orbitals in silicon compounds has led to postulation of these expanded valence intermediates such as the pentacoordinate transition state. Thus the enhanced reactivity at silicon (relative to carbon) is attributed to 3d orbital involvement in reducing the free energy of the transition state.

The use of electron-withdrawing substituents to enhance the rate of displacement at silicon was applied to the aminosilane/silanol polycondensation in an effort to force the polymer chain to higher molecular weight. Specific prior kinetic studies in this laboratory [6] had verified a modest rate enhancement using aminosilane monomers with electron-withdrawing groups.

The model polymer-forming reaction is represented as follows:
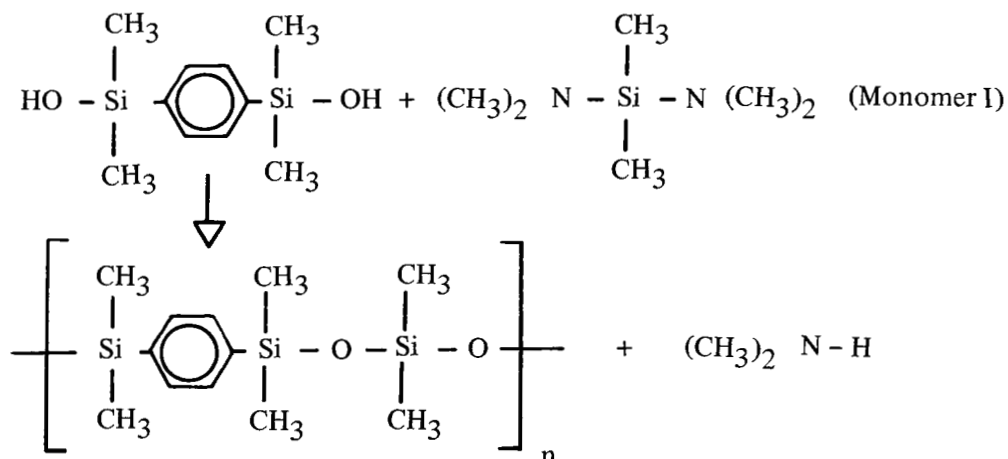
In this reaction mechanism, the displaced $(CH_3)_2 N^-$ anion has little charge stabilizing capability and cannot contribute appreciably to lowering transition state energy. The current study addressed specifically structured aminosilanes with charge delocalization capacity. A series of monomers was synthesized with a nitrogen heterocycle as the leaving group. These monomers were structured progressively toward charge delocalization capacity:
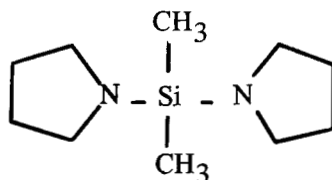
N,N-bis (pyrrolidinyl) dimethylsilane, (Monomer II)

2
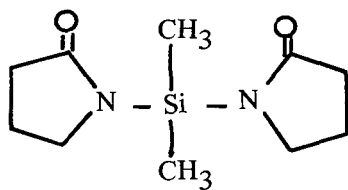
N, N-bis (gamma-butyrolactam) dimethylsilane, (Monomer III)

The leaving group from Monomer III can be stabilized by charge delocalization and should promote more effective nucleophilic displacement:

The compounds I through III are typically synthesized by reaction of dimethyl-dichlorosilane with the corresponding amine derivative.

B. Polymerization Methodology

Stewart [4] utilized both the very reactive bis-ureidosilanes and a multi-stage polymerization technique to generate molecular weights $>10^6$ for the carborane-siloxane system, but the results were not reproducible and were complicated by the extreme moisture sen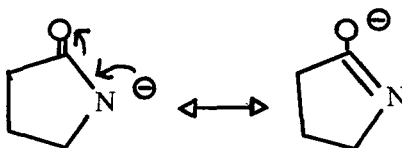sitivity of the ureidosilanes. More recently, Dvornic [7] utilized the ureidosilanes to prepare silphenylene-siloxane polymers but attained only modest molecular weights (<200,000). In the current study, a parallel approach to attainment of very high molecular weight SPS polymers involved investigation of multi-stage polymerization utilizing the basic bis(dimethylamino)dimethylsilane monomer. This approach was based on first synthesizing a silanol-terminated prepolymer, using 90 to 98 percent of the aminosilane stoichiometric equivalence. A series of prepolymers were prepared in this fashion, then isolated and purified by precipitation. They were then chain-extended to higher molecular weights by incremental addition of bis(dimethylamino)dimethylsilane by the following scheme:

(90-98 mol - percent)

(Prepolymer)

$$HO-\left[Si(CH_3)_2-C_6H_4-Si(CH_3)_2-O-Si(CH_3)_2-O\right]_x-Si(CH_3)_2-C_6H_4-Si(CH_3)_2-OH$$

$$(CH_3)_2N-Si(CH_3)-N(CH_3)_2$$

$$\left[Si(CH_3)_2-C_6H_4-Si(CH_3)_2-O-Si(CH_3)_2-O\right]_n \quad n \ggg x$$
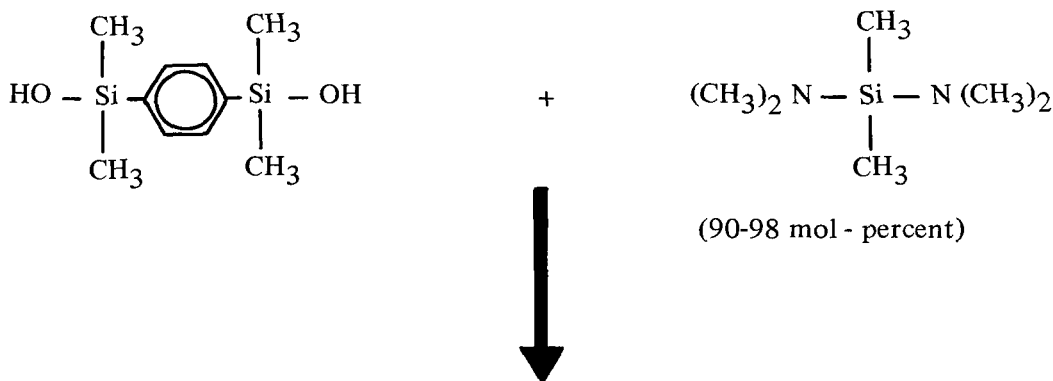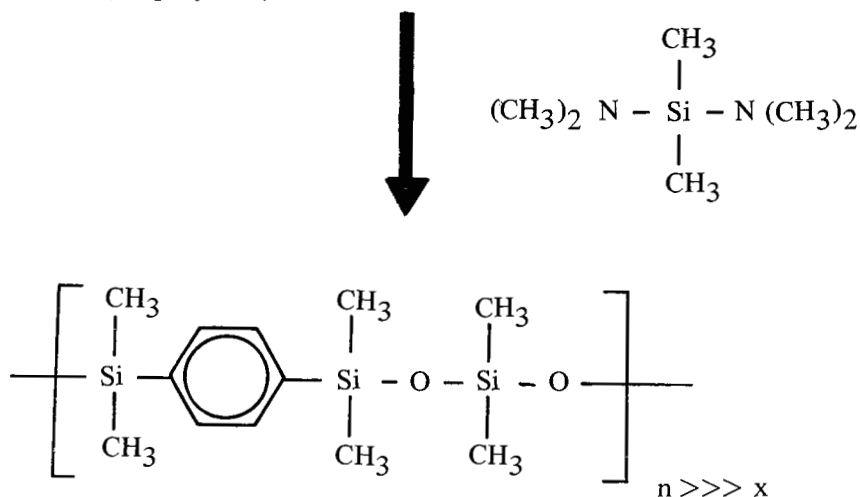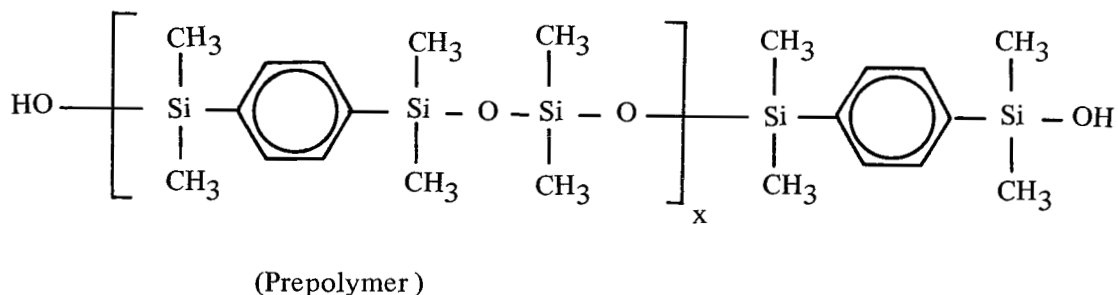
III. EXPERIMENTAL

A. Materials

Toluene (Fisher Scientific) was distilled from calcium hydride under a nitrogen atmosphere and stored over molecular sieves until used. Tetrahydrofuran (Burdick and Jackson), methanol and methylene chloride (Fisher Scientific) were used without further purification. NMR spectra were obtained on a 60 MHz Proton NMR, Varian EM-360L. The purity of 1,4-bis(hydroxydimethylsilyl)benzene (Silar Laboratories) was checked by gel permeation chromatography on a bank of three 100 Å μStyragel columns, with tetrahydrofuran as mobile phase. Material exhibiting less than 98.4 percent purity on the UV absorbance detector was recrystallized twice from boiling carbon tetrachloride. The white crystals melted at 135° to 136°C and exhibited the following nmr spectrum (Fig. 1): 0.07 (s, 12, Si-CH$_3$); 3.41 (s, 2, Si-OH); 7.36 (s, 4, phenyl ring hydrogens) in deuterated acetronitrile (Aldrich Chemical) with methylene chloride as reference. A 3 percent OV17 on 80/100 Chromosorb W gas chromatographic column was used to check the purity of bis(dimethylamino)dimethylsilane (Silar Laboratories), N,N-bis-pyrrolidinyl)dimethylsilane and N,N-bis (gamma-butyrolactam)dimethylsilane (Synmet Inc.). The bis(dimethylamino)dimethylsilane produced the following nmr spectrum (Fig. 2): 0.08 (s, 1, Si-CH$_3$); 2.38 (s, 2, N-CH$_3$) with dry methylene chloride as reference. These silanes were used without further purification.
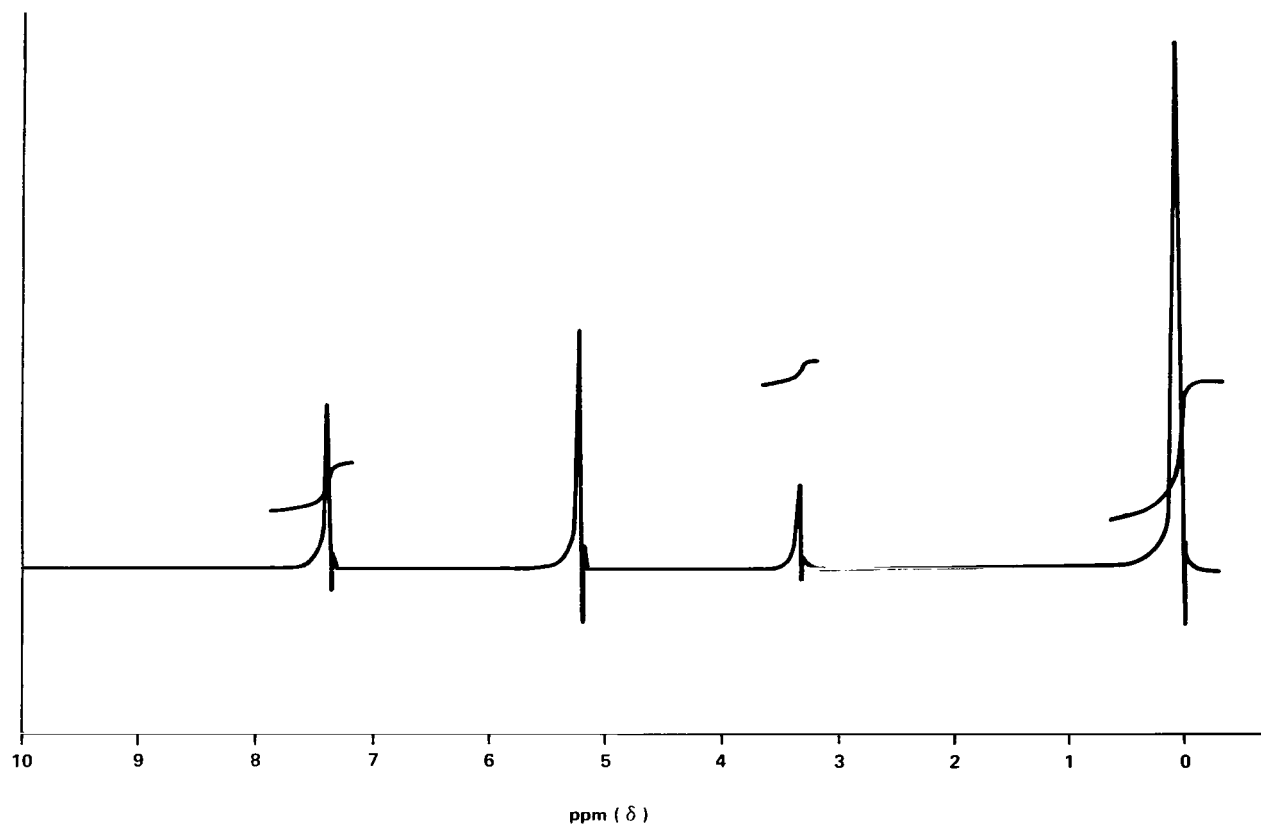
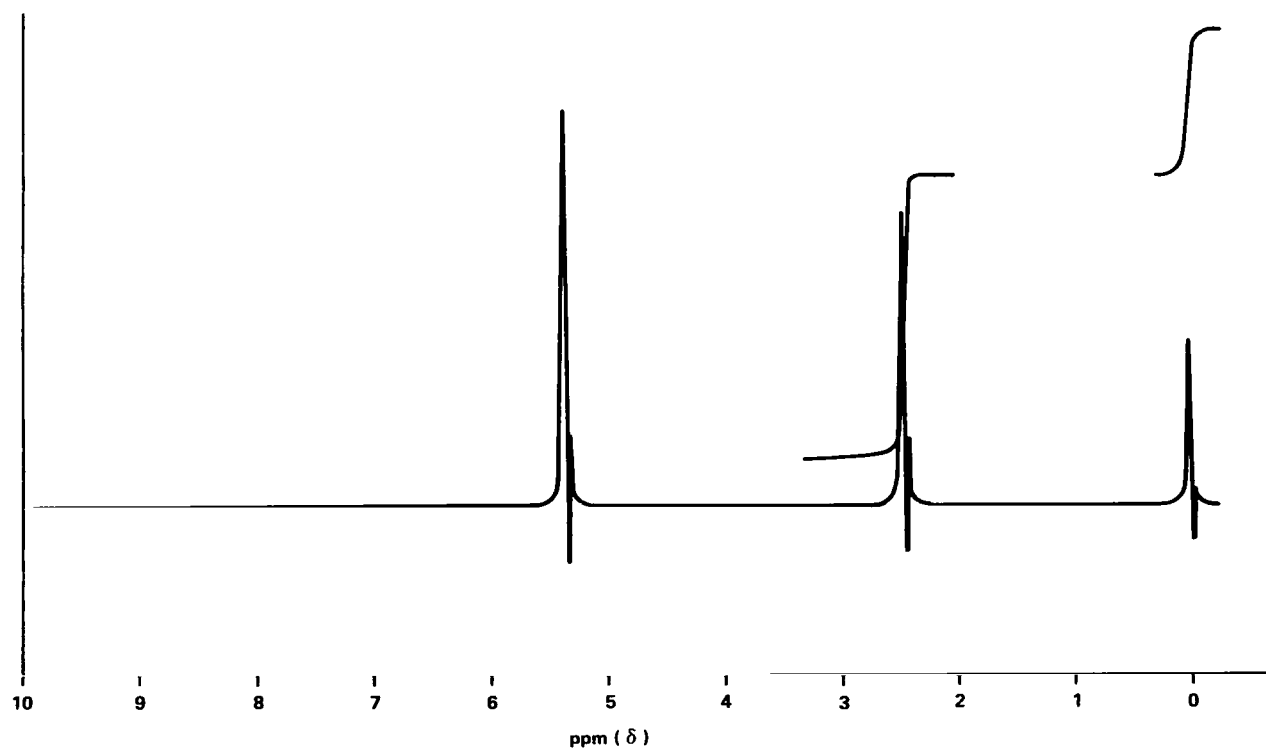Figure 1. NMR spectrum of 1,4-bis(hydroxydimethylsilyl) benzene.

Figure 2. NMR spectrum of bis(dimethylamino) dimethylsilane.

B. Prepolymers

The following is a typical prepolymer preparation. 1,4-Bis(hydroxydimethylsilyl)benzene (50.0 g, 0.221 mol) was placed in a weighed three-necked, 500 mL round bottom flask and dried overnight in a vacuum oven at 50°C. The flask was reweighed, fitted with a reflux condenser, thermometer and addition funnel, then purged with nitrogen. Dry toluene (200 mL) was added through the addition funnel. After additional toluene (40 mL) was placed in the funnel, it was sealed with a rubber septum and a positive nitrogen pressure was established. The reaction mixture was slowly heated to a gentle reflux (109° to 112°C). Under a nitrogen atmosphere, bis(dimethylamino)dimethylsilane (30.9 g, 0.211 mol, 95.5 mol percent) was withdrawn into a dried, preweighed, air-tight syringe and injected through the septum into the toluene in the addition funnel. This solution was added to the reaction mixture over a 6 hr period. After 24 hr the condenser was removed, a distillation head added and 150 mL of toluene was distilled from the reaction mixture. At this time, moist acid-base paper held in the effluent nitrogen indicated reduced amine production. After cooling, the mixture was added dropwise, with rapid stirring, to 800 mL of methanol. The methanol was then decanted; the product, a viscous oil, was dissolved in a few milliliters of methylene chloride and transferred to a sample bottle. A warm water bath and nitrogen stream were used to partially remove the solvent. The product was dried overnight in a vacuum oven at 50°C. A yield of 50.0 g (84 percent based on the amount of silane used) was obtained. This product had an intrinsic viscosity of 0.191 dL/g (THF, 30.1 ± 0.1°C).

C. Polymers

A characteristic polymer synthesis was performed as follows. Prepolymer (49.0 g, 82 percent theoretical yield) was added to a 500 mL three-necked flask and dried overnight in a vacuum oven at 50°C. The system was assembled as for the prepolymer synthesis. Bis(dimethylamino)dimethylsilane (2.13 g, 0.0146 mol), an amount double the 5 mol percent deficiency existing from the prepolymer synthesis, was added, as in the prepolymer procedure, over 4 hr. During this time 200 mL of toluene was added to maintain stirring. Samples (0.1 mL) were withdrawn before each addition of silane and after 24 hr. The samples were precipitated in methanol, dried in a vacuum over at 50°C, dissolved in THF and analyzed by gel permeation chromatography. After 24 hr the solution was cooled, precipitated in methanol (1200 mL), dissolved in tetrahydrofuran (200 mL), reprecipitated in methanol (1000 mL), and dried in a vacuum oven at 50°C for two days. The yield was 44 g (74 percent overall). This product had an intrinsic viscosity of 2.42 dL/g (THF, 30.1 ± 0.1°C).

D. Comparison of Silanes

Three different silanes were used to advance a 95.5 mol percent prepolymer (15 g each trial). Following the previous procedure, either Monomer I, bis(dimethylamino)dimethylsilane (0.72 g, 0.00493 mol); Monomer II, N,N-bis(pyrrolidinyl)dimethylsilane (0.99 g, 0.00500 mol); or Monomer III, N,N-bis(gamma-butyrolactam)dimethylsilane (1.23 g, 0.00544 mol) was added to toluene (40 mL) in an addition funnel. This solution was added to the reaction mixture in four increments at 2 hr intervals. Samples were withdrawn, prepared and analyzed as described in the preceding section. Reaction products were purified and characterized as previously noted.

E. Characterization

Intrinsic viscosities of both prepolymers and polymers were determined in tetrahydrofuran (30.1 ± 0.1°C) using a Cannon-Ubbelohde viscometer. Stock solutions were diluted three times.

Molecular weights and polydispersities were determined on a Waters Associates liquid chromatograph with a bank of two 10^4 Å and two 10^5 Å μSytragel columns, tetrahydrofuran mobile phase and 1.0 mL/min flow rate. A Perkin-Elmer Sigma 15 with GPC 2S software was used for data collection, as well as, for molecular weight and polydispersity calculations. The calibration curve was determined from the product of each standard's peak M and intrinsic viscosity. Experimental molecular weights were derived by dividing out the intrinsic viscosity. Monodisperse polystyrene standards (Waters Associates, 3.45×10^4 to 1.75×10^6 peak M's) provided the calibration curve (Table 1). These standards were mixed as a single solution and injected each day before analyzing an experimental material. This guarded against day-to-day fluctuations in the chromatographic system. Samples of three polymers were submitted to an independent laboratory, ArRo Laboratories, for analysis by membrane osmometry and light scattering.

TABLE 1. CALIBRATION DATA FOR STANDARD POLYSTYRENES

Peak M[a]	Intrinsic Viscosity[b] $[\eta]$ (dL/g)	(Peak M) x $[\eta]$	Retention Time[c] (min)
2.3×10^6	4.92	1.13×10^7	22.81[d]
1.75×10^6	3.11	5.44×10^6	23.46
6.55×10^5	1.86	1.22×10^6	25.31
3.70×10^5	1.26	4.66×10^5	26.87
1.96×10^5	0.727	1.42×10^5	29.38
1.11×10^5	0.521	5.78×10^4	30.79
3.45×10^4	0.231	7.97×10^3	34.63

a. Values supplied by Waters Associates.
b. THF (30.1 ± 0.1°C).
c. Retention times reproducible to ± 0.5 min.
d. Determined separately.

F. Thermal Analysis

A DuPont 1090 Thermal Analyzer with 951 Thermogravimetric Analyzer Module was used to acquire thermogravimetric analyses of three experimental polymers (weight average molecular weights of: 5.1×10^5, 8.9×10^5, 1.1×10^6) and two commercial resins (General Electric SE 5211 and RTV 560). Gradient (20 deg/min, 25 to 700°C and isothermal (400°C for 24 hr) analyses were conducted in both air and nitrogen. Before analysis the commercial resins were extracted with methylene chloride, centrifuged and decanted, filtered and dried in a vacuum oven at 30°C overnight. Results are shown in Figures 3 through 8. Glass transition temperatures for one experimental polymer (weight average molecular weight of 1.1×10^6) and the two commercial resins were determined with a 910 Differential Scanning Calorimeter System.

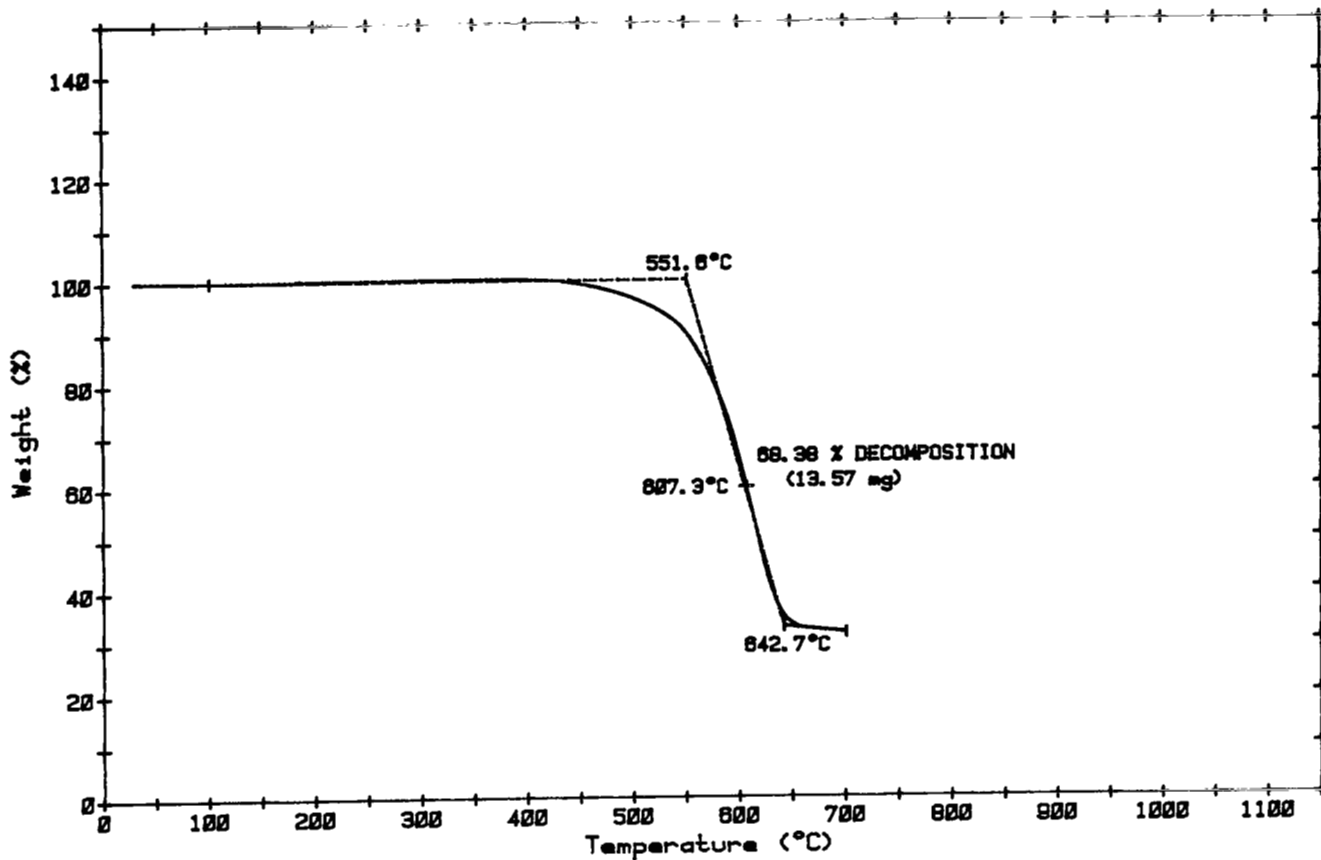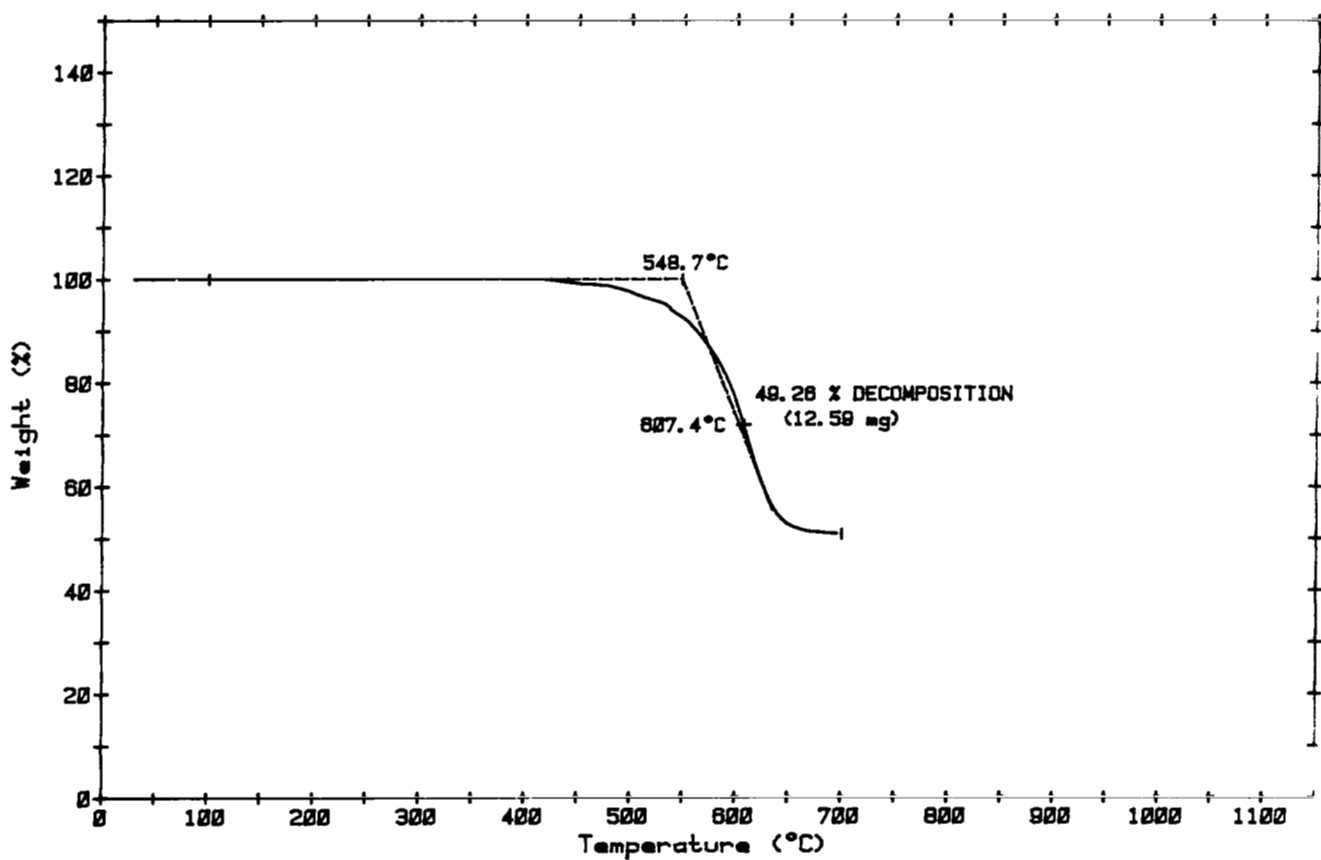Figure 3. TGA for SPS polymer in nitrogen.

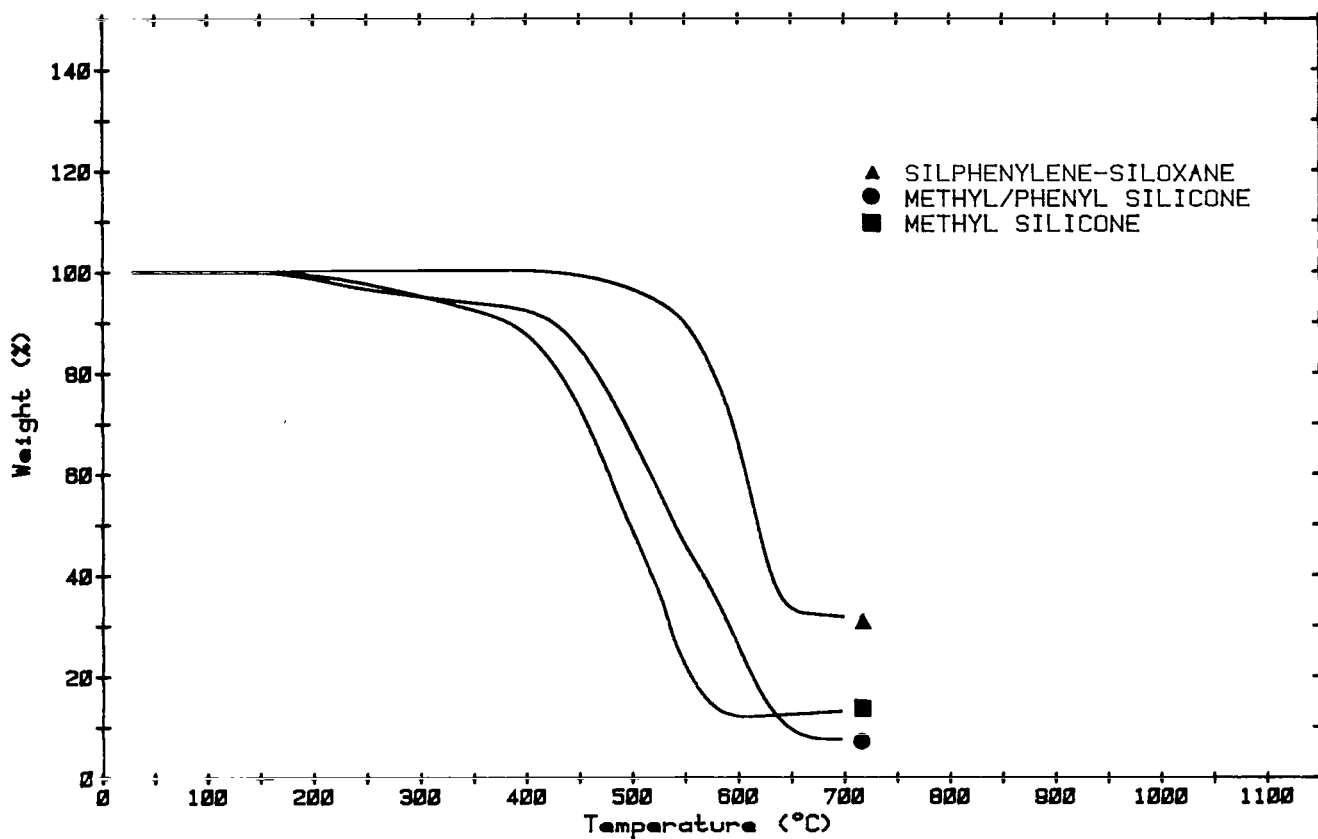Figure 4. TGA for SPS polymer in air.

Figure 5. Comparative TGA for SPS polymer versus commercial silicones in nitrogen.
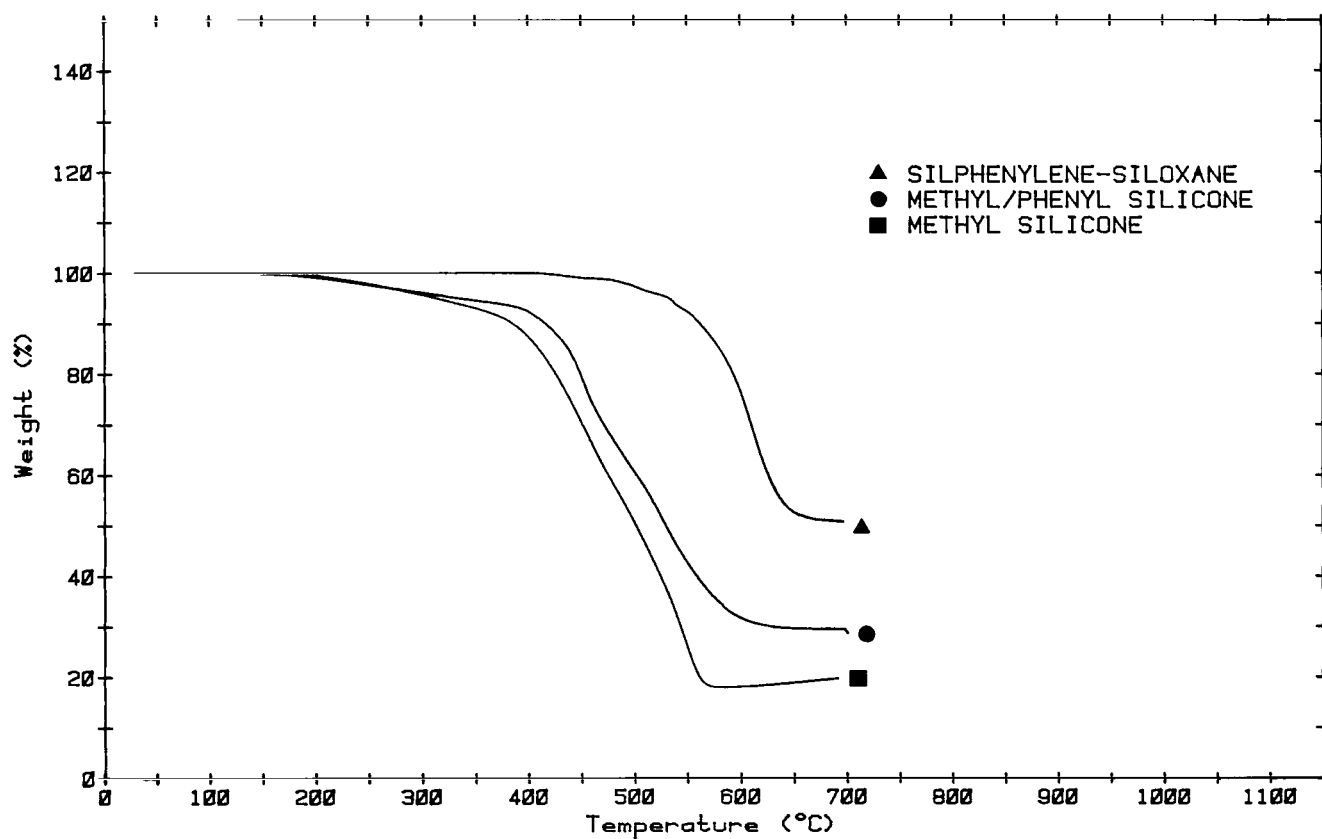

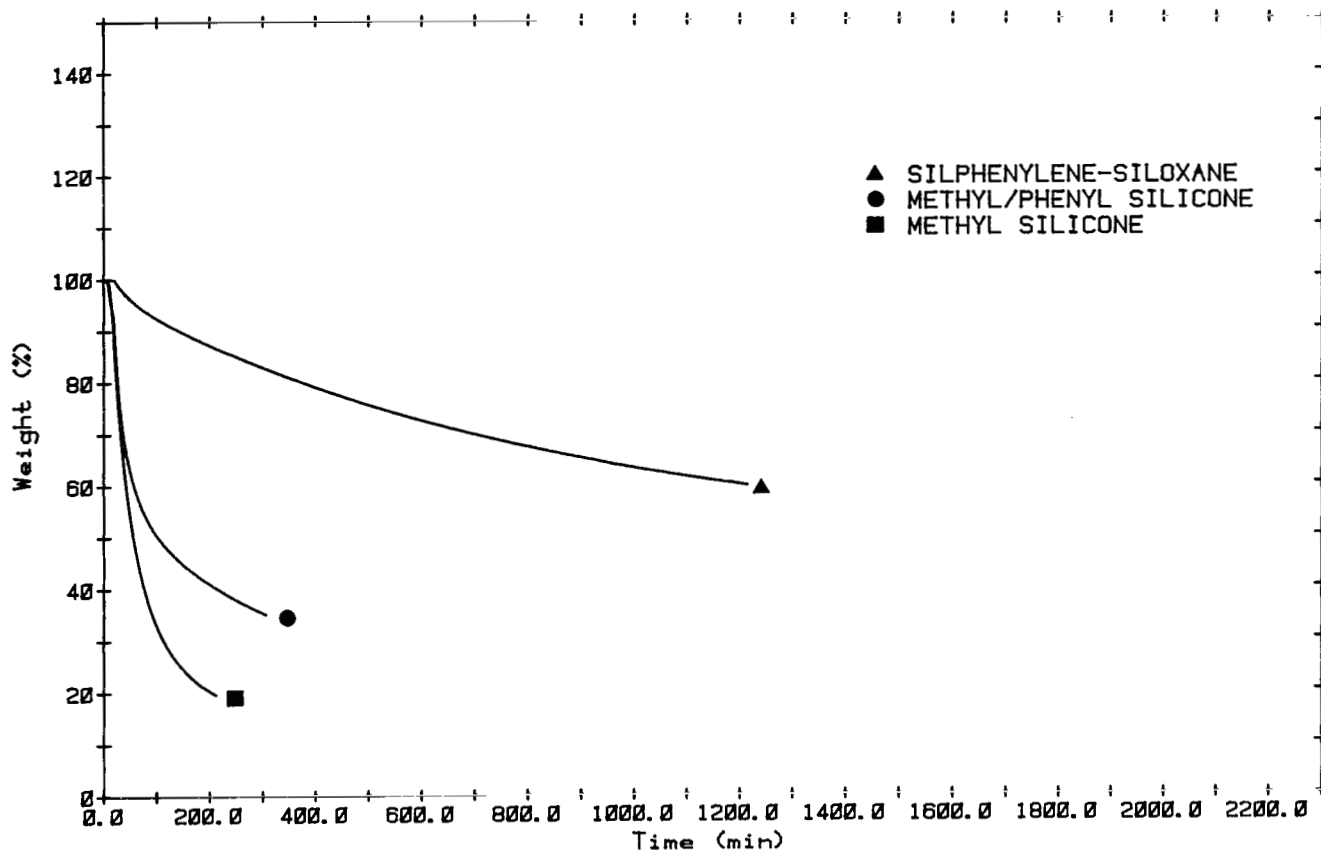Figure 6. Comparative TGA for SPS polymer versus commercial silicones in air.

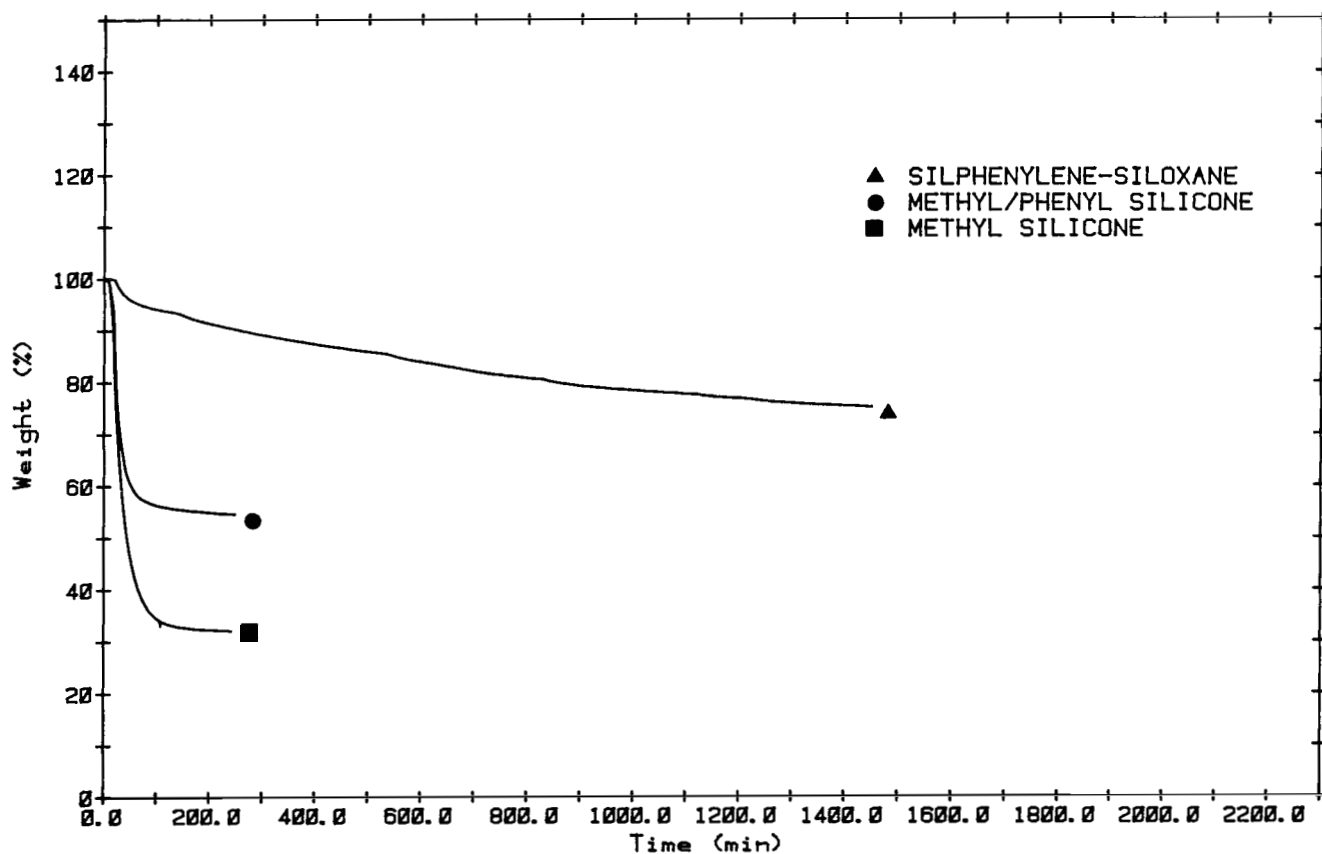Figure 7. Isothermal TGA for SPS polymer versus commercial silicones in nitrogen.

Figure 8. Isothermal TGA for SPS polymer versus commercial silicones in air.

10

IV. RESULTS AND DISCUSSION

Both the reactive monomer and two-stage polymerization approaches (as described in Section II) were exploited in this study, with the latter being far more successful. The use of either N,N-bis(pyrrolidinyl)dimethylsilane (Monomer II) or N,N-bis(gamma-butyrolactam) dimethylsilane (Monomer III) resulted in only modest advancement in polymer molecular weight as compared to the standard Monomer I, bis(dimethylamino)dimethylsilane. As indicated by comparison of GPC retention times in Table 2, the presumed enhancement of nucleophilic reactivity for Monomer III was not manifested in the polymer-forming reaction. Indeed, some degradation apparently occurred, resulting in lower molecular weights. Monomer III was obviously more reactive than I or II, as observed by its increased moisture sensitivity. However, this same enhanced reactivity apparently results in undesirable side reactions leading to polymer degradation.

The multi-stage polymerization approach to high molecular weight SPS polymers produced very encouraging results. The data in Table 3 typify the molecular weight characteristics of both prepolymers and the derived high polymers. Generation of prepolymers from 95 to 96 mol-percent aminosilane appeared to result in the highest $\overline{M}_w$ (1.1×10^6 to 1.2×10^6). These results, determined by GPC techniques, satisfy the original goals of the study and represent the first reported attainment of molecular weights in excess of one million for this class of condensation polymer.

The molecular weights for three of the SPS polymers were also determined by an independent testing laboratory (ArRo Laboratories) utilizing different analytical techniques (Table 4). These results verify the attainment of very high molecular weights, with light scattering measurements of $\overline{M}_w$ as high as 2.3×10^6 for one of the SPS samples. An additional significant feature is that scale-up of the high molecular weight runs to at least 50 gram quantities was demonstrated (Table 3). This provided large enough samples for compounding and cure studies in a follow-on effort. The success of the multi-stage technique is believed due to more effective control of polymerization stoichiometry. The aminosilane monomer (b. 127°C) has appreciable vapor pressure at toluene reflux conditions and some material is undoubtedly lost via the nitrogen purge in the polymerization reactor. Isolation and purification of the silanol-terminated prepolymer as an intermediate step allows a small quantity of fresh aminosilane monomer to be introduced in a carefully controlled fashion to extend the prepolymer chains. The dramatic increase in viscosity (and molecular weight) accompanying the conversion of prepolymer to high polymer is convincing evidence of the efficiency of this procedure.

The SPS polymers were thermally characterized, primarily by TGA techniques, to assess their overall thermal/oxidative stability and to determine if a relation exists between molecular weight and thermal performance. Figures 3 and 4 illustrate the thermal stability of the SPS system in nitrogen and air. The onset of decomposition occurred at nearly the same temperature, whether air or nitrogen was used.

The lower overall weight loss in air (49.26 percent) is believed due to oxidative conversion to highly stable SiO_2. The SPS polymer was also compared to commercial silicones, represented by methylphenyl-silicone and dimethylsilicone structures. The comparative TGA data are presented in Figures 5 and 6, demonstrating that the SPS polymer is far superior in thermal stability. This has been attributed to the presence of the in-chain 1,4-phenylene moiety, which inhibits the formation of cyclic siloxane trimer and tetramer (a predominant thermal degradation mechanism for conventional silicones). The relative thermal stability of the SPS system was further demonstrated by isothermal exposure at 400°C (Figs. 7 and 8). The commercial silicones were degraded rapidly under these conditions.

11

TABLE 2. SILANE REACTIVITY IN POLYMER MOLECULAR WEIGHT ADVANCEMENT

Reaction Time (Hrs.)	Percent Silane Added	Retention Time,[a] Minutes		
		Monomer I	Monomer II	Monomer III
0	0	34.9	36.3	36.3
2	25	30.7	29.3	29.9
4	50	25.9	25.9	30.9
6	75	25.5	25.5	29.1
8	100	–	25.5	30.1
22	–	25.1	25.5	30.9
26	–	–	25.5	30.9

a. Taken from GPC runs; shorter retention times are indicative of higher molecular weight.

TABLE 3. PREPOLYMER/POLYMER MOLECULAR WEIGHT DATA

Prepolymers			Polymers	
Silane Mol%	Viscosity $[\eta]$ (dL/g)	$\overline{M}_w{}^a$	Viscosity $[\eta]$ (dL/g)	$\overline{M}_w{}^a$
91.9	0.131	1.6×10^4	1.56	5.0×10^5
95.5	0.153	2.1×10^4	3.11	1.2×10^6
95.5[b]	0.181	2.2×10^4	2.50	6.2×10^5
95.6[b]	0.191	3.6×10^4	2.42[b]	1.1×10^6

a. Determined by gel permeation chromatography.
b. 50 gram scale-up.

TABLE 4. COMPARISON OF GPC MOLECULAR WEIGHT DATA WITH ALTERNATE TECHNIQUES

	Weight Average		Number Average	
Polymer	GPC	L. S.[a]	GPC	M. O.[b]
SPS-1	1.1×10^6	2.3×10^6	2.5×10^5	1.9×10^5
SPS-2	8.9×10^5	8.8×10^5	1.1×10^5	9.6×10^4
SPS-3	5.1×10^5	4.8×10^5	1.8×10^5	5.7×10^4

a. Light scattering technique (ArRo Laboratories).
b. Membrane osmometry technique (ArRo Laboratories).

Comparison of thermal data from the SPS polymers over the molecular weight range of 5.1×10^5 to 1.1×10^6 indicated no significant correlation of $\overline{M}_w$ with thermal stability. This lack of correlation was also true for the glass transition temperature (T_g) of the SPS polymers, where the T_g was determined by DSC techniques (Fig. 9) to occur at -50 to $-55°C$, independent of the increases in polymer molecular weight. The bulky phenylene substituent in the SPS polymer chain restricts chain flexibility and maintains the T_g at a relatively high temperature compared to the commercial silicone (Fig. 9).
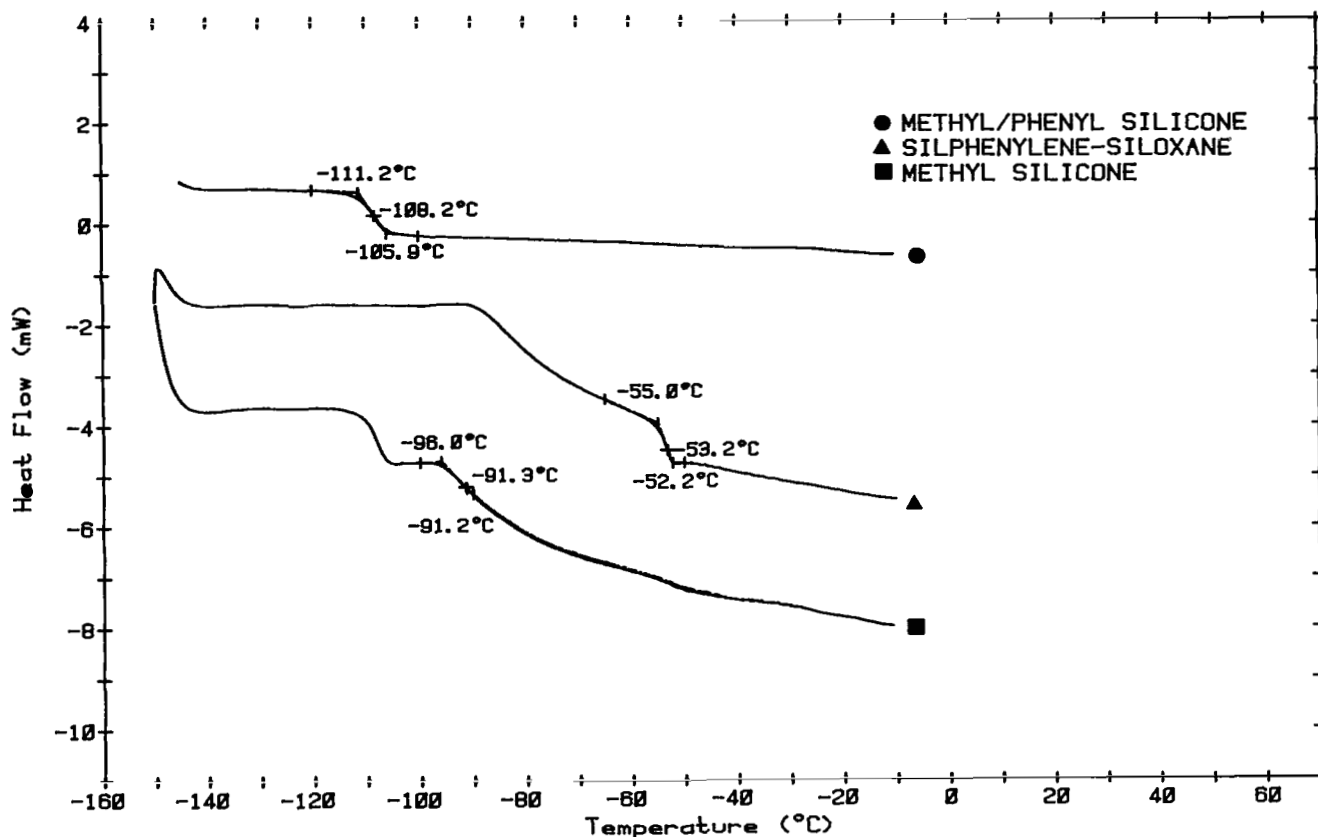

Figure 9. Comparative DSC for SPS polymer versus commercial silicones.

V. CONCLUSIONS AND RECOMMENDATIONS

The initial goal of development of polymerization methodology for SPS polymers with molecular weights approaching 10^6 was met. The multi-stage polymerization methodology involving preparation/ isolation of a silanol-terminated prepolymer and subsequent chain extension with additional aminosilane monomer proved to be an effective route to formation of ultrahigh molecular weight polymer. Scale-up to 50 gram quantities with retention of high $\overline{M}_w$ was demonstrated.

Any extension of this study should focus on formulation/cure technology for the SPS polymer system, via incorporation of appropriate vulcanization sites along the polymer chain. This will provide vulcanized elastomer samples whose mechanical properties can be fully evaluated.

13

REFERENCES

1. Patterson, W. J. and Morris, D. E.: Journal of Polymer Science. Vol. 10, 1972, p. 169.

2. Pittman, C. U., Patterson, W. J. and McManus, S. P.: Journal of Polymer Science. Vol. 14, 1976, p. 1715.

3. Patterson, W. J., McManus, S. P. and Pittman, C. U.: Macromolecular Syntheses. Vol. 6, 1977, p. 99.

4. Stewart, D. D.: Macromolecules. Vol. 12, 1979, p. 373.

5. Sommer, L. H.: Stereochemistry, Mechanism and Silicon. McGraw-Hill, New York, 1965, p. 149.

6. McManus, S. P., Patterson, W. J. and Pittman, C. U.: Journal of Polymer Science. Vol. 12, 1974, p. 825.

7. Dvornic, P. R. and Lenz, R. W.: Journal of Polymer Science, Polymer Chemistry Edition. Vol. 20, 1982, p. 593.

1. REPORT NO. NASA TP-2295	2. GOVERNMENT ACCESSION NO.	3. RECIPIENT'S CATALOG NO.
4. TITLE AND SUBTITLE Ultra-High Molecular Weight Silphenylene-Siloxane Polymers		5. REPORT DATE March 1984
		6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) W. J. Patterson, N. H. Hundley, and L. M. Ludwick		8. PERFORMING ORGANIZATION REPORT #
9. PERFORMING ORGANIZATION NAME AND ADDRESS George C. Marshall Space Flight Center Marshall Space Flight Center, Alabama 35812		10. WORK UNIT, NO. M-441
		11. CONTRACT OR GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS National Aeronautics and Space Administration Washington, D.C. 20546		13. TYPE OF REPORT & PERIOD COVERED Technical Paper
		14. SPONSORING AGENCY CODE

15. SUPPLEMENTARY NOTES

Prepared by Materials and Processes Laboratory, Science and Engineering Directorate

16. ABSTRACT

Silphenylene-siloxane copolymers with molecular weights above one million were prepared using a two-stage polymerization technique. The technique was successfully scaled up to produce 50 grams of this high polymer in a single run. The reactive monomer approach was also investigated using the following aminosilanes: bis (dimethylamino)dimethylsilane, N, N-bis(pyrrolidinyl)dimethylsilane and N, N-bis (gamma-butyrolactam)dimethylsilane). Thermal analyses were performed in both air and nitrogen. The experimental polymers decomposed at 540° to 562°C, as opposed to 408° to 426°C for commercial silicones. Differential scanning calorimetry showed a glass transition (Tg) at -50° to -55°C for the silphenylene-siloxane copolymer while the commercial silicones had Tg's at -96° to -112°C.

17. KEY WORDS Elastomer Polymer Silicone Siloxane Silphenylene-Siloxane Thermal degradation	18. DISTRIBUTION STATEMENT Unclassified-unlimited STAR Category: 27	
19. SECURITY CLASSIF. (of this report) Unclassified	20. SECURITY CLASSIF. (of this page) Unclassified	21. NO. OF PAGES 19	22. PRICE A01

NASA

2   1 1U,C,   840314 S00903DS
DEPT OF THE AIR FORCE
AF WEAPONS LABORATORY
ATTN: TECHNICAL LIBRARY (SUL)
KIRTLAND AFB NM 87116